



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# A Comparison of the Corrosion Resistance of Iron-Based Amorphous Metals and Austenitic Alloys in Synthetic Brines at Elevated Temperature

J. C. Farmer

December 15, 2008

MRS Fall Meeting 2008  
Boston, MA, United States  
December 1, 2005 through December 5, 2005

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

# **A Comparison of the Corrosion Resistance of Iron-Based Amorphous Metals and Austenitic Alloys in Synthetic Brines at Elevated Temperature**

Joseph Farmer<sup>1</sup>

<sup>1</sup>Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

## **ABSTRACT**

Several hard, corrosion-resistant and neutron-absorbing iron-based amorphous alloys have now been developed that can be applied as thermal spray coatings. These new alloys include relatively high concentrations of Cr, Mo, and W for enhanced corrosion resistance, and substantial B to enable both glass formation and neutron absorption. The corrosion resistances of these novel alloys have been compared to that of several austenitic alloys in a broad range of synthetic brines, with and without nitrate inhibitor, at elevated temperature. Linear polarization and electrochemical impedance spectroscopy have been used for *in situ* measurement of corrosion rates for prolonged periods of time, while scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) have been used for *ex situ* characterization of samples at the end of tests. The application of these new coatings for the protection of spent nuclear fuel storage systems, equipment in nuclear service, steel-reinforced concrete will be discussed.

## **INTRODUCTION**

The outstanding corrosion resistance that may be possible with amorphous metals was recognized several years ago [1-3]. Compositions of several Fe-based amorphous metals were published, including several with very good corrosion resistance. Examples included: thermally sprayed coatings of Fe-10Cr-10-Mo-(C,B), bulk Fe-Cr-Mo-C-B, and Fe-Cr-Mo-C-B-P [4-6]. The corrosion resistance of an Fe-based amorphous alloy with yttrium (Y), Fe<sub>48</sub>Mo<sub>14</sub>Cr<sub>15</sub>Y<sub>2</sub>C<sub>15</sub>B<sub>6</sub> was also been established [7-9]. Yttrium was added to this alloy to lower the critical cooling rate. Several nickel-based amorphous metals were developed that exhibit exceptional corrosion performance in acids, but are not considered in this study, which focuses on Fe-based amorphous metals. Thermal spray coatings of crystalline nickel-based alloy coatings have been deposited with thermal spray technology, but appear to have less corrosion resistance than comparable nickel-based amorphous metals [10]. Two Fe-based amorphous alloys have been found with exceptional corrosion resistance compared to other such Fe-based amorphous alloys, and can be applied as a protective thermal spray coating: SAM2X5 (Fe<sub>49.7</sub>Cr<sub>17.7</sub>Mn<sub>1.9</sub>Mo<sub>7.4</sub>W<sub>1.6</sub>B<sub>15.2</sub>C<sub>3.8</sub>Si<sub>2.4</sub>)

and SAM1651 ( $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$ ). These materials incorporate chromium (Cr), molybdenum (Mo) and tungsten (W) for enhanced corrosion resistance, boron (B) to enable glass formation and neutron absorption, and yttrium (Y) for lower critical cooling rates [11-17]. SAM2X5 appears have significantly better corrosion resistant than its Mo-deficient parent alloy ( $\text{Fe}_{52.3}\text{Cr}_{19}\text{Mn}_2\text{Mo}_{2.5}\text{W}_{1.7}\text{B}_{16}\text{C}_4\text{Si}_{2.5}$ ).

## **EXPERIMENTAL**

### **Thermal spray coatings**

The coatings discussed here were made with the high-velocity oxy-fuel (HVOF) process, which involves a combustion flame, and is characterized by gas and particle velocities that are three to four times the speed of sound (mach 3 to 4). This process is ideal for depositing metal and cermet coatings, which have typical bond strengths of 5,000 to 10,000 pounds per square inch (5-10 ksi), porosities of less than one percent ( $< 1\%$ ) and extreme hardness. The cooling rate that can be achieved in a typical thermal spray process such as HVOF are on the order of ten thousand Kelvin per second ( $10^4$  K/s), and is high enough to enable many alloy compositions to be deposited above their respective critical cooling rate, thereby maintaining the vitreous state. However, the range of amorphous metal compositions that can be processed with HVOF is more restricted than those that can be produced with melt spinning, due to the differences in achievable cooling rates. Both kerosene and hydrogen have been investigated as fuels in the HVOF process used to deposit SAM2X5 and SAM1651.

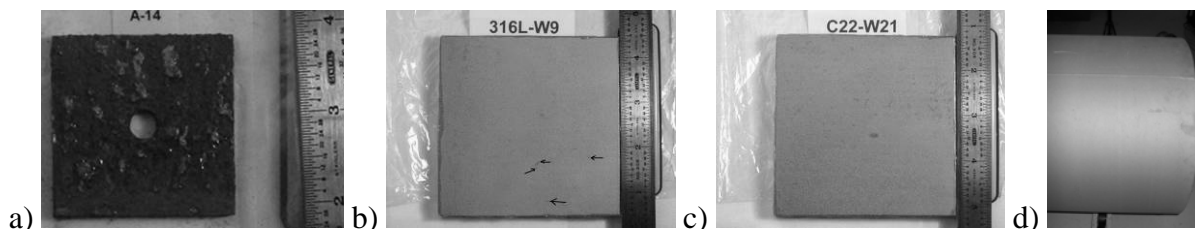
### **X-ray diffraction**

X-ray diffraction (XRD) measurements of SAM2X5 and SAM1651 gas atomized powders and HVOF coatings has been performed, verifying that both the feed powder, as well as the final thermal spray coatings were indeed amorphous. In general, a broad halo is observed at  $2\theta \sim 44^\circ$  which indicates that these coatings was predominately amorphous [21-22]. In cases where very small sharp peaks are observed with SAM2X5, they are generally attributed to the presence of minor crystalline phases including  $\text{Cr}_2\text{B}$ , WC,  $\text{M}_{23}\text{C}_6$  and bcc ferrite, which are known to have a detrimental effect on corrosion performance. These potentially deleterious precipitates deplete the amorphous matrix of those alloying elements, such as chromium, responsible for enhanced passivity. Coatings with less residual crystalline phase have been observed.

### **Salt fog testing**

Several reference samples and amorphous-metal coatings have been made and subjected to salt fog testing. Salt fog tests were conducted according to the standard General Motors (GM) salt fog test, identified as GM9540P. Figure 1 shows the condition of several samples after testing: (a) 1018 carbon steel reference specimens; (b) an HVOF SAM2X5 coating on Type 316L stainless steel, (c) an HVOF SAM2X5 coating on Ni-based Alloy C-22 and (d) an HVOF

SAM2X5 coating on half-scale spent nuclear fuel (SNF) container made of Type 316L stainless steel, all after 8 full cycles in GM salt fog test. Clearly, the thermal-spray coatings of SAM2X5 have good resistance to corrosive attack in such environments. Similar testing was done with SAM1651 with similar positive results.



**Figure 1.** Photographs of (a) 1018 Steel, (b) SAM2X5 on 316L, (c) SAM2X5 on C-22 and (d) SAM2X5 on prototype spent nuclear fuel container.

### **Immersion testing**

Linear polarization, weight-loss and dimensional-change measurements have been made to determine the rates of corrosion of SAM2X5 and SAM1651 HVOF coatings in a wide variety of synthetic brines including but not limited to: natural seawater at 90°C; 3.5-molal NaCl solution at 30°C and 90°C; 3.5-molal NaCl and 0.525-molal KNO<sub>3</sub> solution at 90°C; SDW (simulated dilute water) at 90°C; SCW (simulated concentrated water) at 90°C; and SAW (simulated acidic water) at 90°C. Data for testing in heated seawater and sodium chloride brines, with and without nitrate inhibitor are reported here.

In regard to the SAM2X5 coating, the worst corrosive attack occurred in 3.5m NaCl without nitrate inhibitor at 90°C. The corrosive attack of coated rods and plates is shown in Figures 2 and 3, respectively. The addition of nitrate was observed to be very effective in mitigating corrosive attack of the SAM2X5 coating in these near-boiling brines.

The optimized SAM1651 coating experienced less corrosion in these aggressive environments than the SAM2X5, as shown in Figures 4 and 5. The corrosion performance demonstrated by this amorphous metal coating appears to be outstanding. As shown in Figure 6, in the case of near-boiling seawater, virtually all corrosion spots could be prevented through the use of an inorganic sealant with the thermal spray coating. The demonstrated performance is comparable to, or better than that of Fe- and Ni-based austenitic steels.

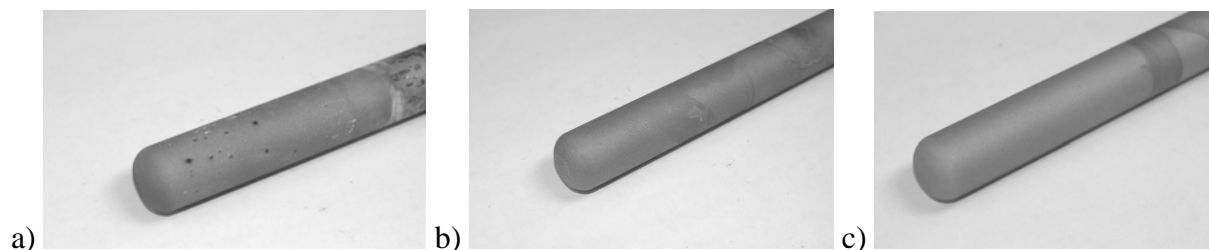
Relative corrosion rates based upon linear polarization measurements of SAM2X5 and SAM1651 are respectively: (a) 5-7 and 4-5  $\mu\text{m/yr}$  in natural seawater at 90°C; (b) 71-116 and 4-5  $\mu\text{m/yr}$  in 3.5-molal NaCl solution at 90°C; and (c) 2 and 6  $\mu\text{m/yr}$  in 3.5-molal NaCl with 0.525-molal KNO<sub>3</sub> solution at 90°C. The corrosion rate for SAM1651 in the 3.5-molal NaCl solution was far less than that for SAM2X5, which is consistent with the discussion of Figures 2 through 6. Figure 7 shows that corrosion, when it does occur, does not penetrate to the substrate.



**Figure 2.** Examples of corrosive attack of optimized HVOF SAM2X5 coatings on rods used for linear polarization and electrochemical impedance spectroscopy after several months in (a) natural seawater 90°C, (b) 3.5m NaCl at 90°C, and (c) 3.5m NaCl + 0.525m KNO<sub>3</sub> 90°C.



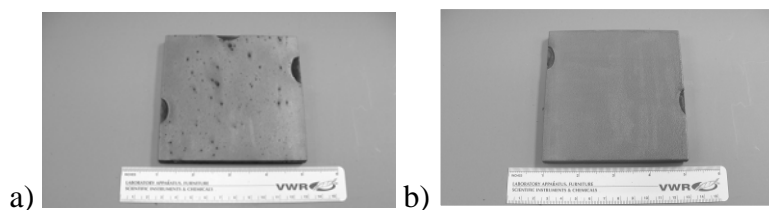
**Figure 3.** Examples of corrosive attack of optimized HVOF SAM2X5 coatings on flat plates after several months in (a) natural seawater at 90°C, (b) 3.5m NaCl at 90°C, and (c) 3.5m NaCl + 0.525m KNO<sub>3</sub> 90°C. Near boiling seawater proved to be the most aggressive aqueous environment of those tested.



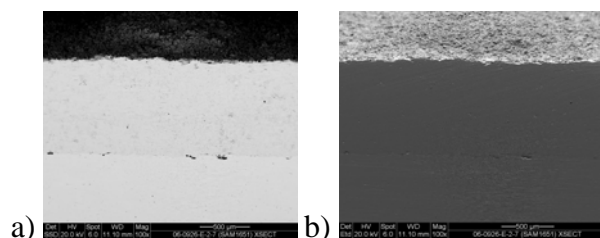
**Figure 4.** Examples of corrosive attack of optimized HVOF SAM1651 coatings on rods used for linear polarization and electrochemical impedance spectroscopy after several months in (a) natural seawater 90°C, (b) 3.5m NaCl at 90°C, and (c) 3.5m NaCl + 0.525m KNO<sub>3</sub> 90°C.



**Figure 5.** Examples of corrosive attack of optimized HVOF SAM1651 coatings on flat plates after several months in (a) natural seawater at 90°C, (b) 3.5m NaCl at 90°C, and (c) 3.5m NaCl + 0.525m KNO<sub>3</sub> 90°C. Near boiling seawater proved to be the most aggressive aqueous environment of those tested.



**Figure 6.** Benefits of using inorganic sealant with optimized HVOF SAM1651 coatings on flat plates after several months in natural seawater at 90°C (a) without sealant and (b) with sealant.



**Figure 7.** Un-Optimized SAM1651 Coating After Approximately Four Months in 90°C Natural Seawater: (a) Back-Scattered Electron Image – BEI and (b) Secondary Electron Image – SEI.

## CONCLUSIONS

Early Fe-based amorphous metal coatings had very poor corrosion resistance and failed salt-fog tests. The HPCRM Program has developed new Fe-based amorphous-metal alloys with good corrosion resistance, high hardness, and exceptional absorption cross-sections for thermal neutrons. More than forty high-performance Fe-based amorphous alloys were systematically designed and synthesized. Cr, Mo and W were added to enhance corrosion resistance; Y was added to lower the critical cooling rate; and B was added to render the alloy amorphous and to enhance capture thermal neutrons. Enriched boron could be used for the further enhancement of the absorption of thermal neutrons. The most profound observations are that the optimized SAM1651 HVOF coating is far more corrosion resistant than the SAM2X5 coating in the most aggressive environment, 3.5 molal NaCl solution without nitrate inhibitor, and that the nitrate anion suppresses corrosive attack of the SAM2X5 coating in concentrated chloride solutions.

## ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Work was co-sponsored by the Office of Civilian and Radioactive Waste Management (OCRWM) of the United States Department of Energy (DOE), and the Defense Science Office (DSO) of the Defense Advanced Research Projects Agency (DARPA). The guidance of Jeffrey Walker at DOE OCRWM and Leo Christodoulou at DARPA DSO is gratefully acknowledged. The production of gas atomized powders by The NanoSteel Company and Carpenter Powder Products, and the production of coatings from these powders by Plasma Technology Incorporated and Caterpillar are gratefully acknowledged. Laboratory work by S. Daniel Day is gratefully acknowledged.

## REFERENCES

1. M. Telford, *Materials Today*, 3 (2004) 36-43.
2. N. Sorensen, R. Diegle, *Corrosion, Metals Handbook*, 9<sup>th</sup> Ed., Vol. 13, J. R. Davis, J. D. Destefani, Eds., ASME, 1987, pp. 864-870
3. D. Polk, B. Giessen, *Metallic Glasses*, J. Gilman, H. Leamy, Eds., ASME, 1978, pp. 2-35
4. K. Kishitake, H. Era, F. Otsubo, *J. Thermal Spray Tech.* 5, 2 (1996) 145-153.
5. S. Pang, T. Zhang, K. Asami, A. Inoue, *Materials Transactions* 43, 8 (2002) 2137-2142.
6. S. Pang, T. Zhang, K. Asami, A. Inoue, *Acta Materialia* 50 (2002) 489-497.
7. F. Guo, S. Poon, G. Shiflet, *Metallic Applied Physics Letters*, 83, 13 (2003) 2575-2577.
8. Z. Lu, C. Liu, W. Porter, *Metallic Applied Physics Letters*, 83, 13 (2003) 2581-2583.
9. V. Ponnambalam, S. Poon, G. Shiflet, *JMR* 19, 5 (2004) 1320.
10. D. Chidambaram, C. Clayton, M. Dorfman, *Surf. Coatings Tech.* 176 (2004) 307-317.
11. J. Farmer et al., *JMR* 22, 8 (2007) 2297-2311.
12. J. Farmer et al., *Critical Factors in Localized Corrosion* 5, N. Missert, Ed., *Electrochem. Soc. Trans.* 3 (2006).
13. J. Farmer et al., *Sci. Basis Nucl. Waste Mgmt. XXX*, MRS Symp. Series, Vol. 985, 2006.
14. J. Farmer et al., *PVP2006-ICPVT11-93835*, ASME, New York, NY, 2006
15. J. Farmer et al. *PVP2005-71664*, ASME, New York, NY, 2005.
16. D. Branagan, U.S. Pat. Appl. No. 20040250929, Filed Dec. 16, 2004.
17. D. Branagan, U.S. Pat. Appl. No. 20040253381, Filed Dec. 16, 2004.
18. T. Lian et al., *Sci. Basis Nucl. Waste Mgmt. XXX*, MRS Symp. Series, Vol. 985, 2006.
19. J-S. Choi et al., *Sci. Basis Nucl. Waste Mgmt. XXX*, MRS Symp. Series, Vol. 985, 2006.
20. J. C. Farmer, *J. Nucl. Tech.* 161, 2 (2008) 169-189.
21. C. K. Saw, *Nanotechnologies for the Life Science*, Challa Kumar, Ed., Wiley-VCH Verlag GmbH and Company, KGaA, Weinheim, 2006.
22. C. K. Saw, R. B. Schwarz, *J. Less-Common Metals*, 140 (1988) 385-393.